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54) PRODUCTION METHOD OF ANTIMICROBIAL COATING FILMS

(57) Abstract

Task

It is intended to provide a production method capable of obtaining coating films where silver or copper as an antimicrobial component is sufficiently and homogeneously dispersed in the inner part.

Solution means

It is characterized in that in the method for producing antimicrobial coating films, an antimicrobial aqueous solution containing silver ions or copper ions and a reducing agent is coated on the surface of unbaked coating films, followed by baking the coating films to reduce the silver ions or copper ions.

CLAIM

1. A production method of antimicrobial coating films, characterized in that in the method for producing antimicrobial coating films, an antimicrobial aqueous solution containing silver ions or copper ions and a reducing agent is coated on the surface of unbaked coating films, followed by baking the coating films to reduce the silver ions or copper ions.

DETAILED EXPLANATION OF THE INVENTION

[0001]

Technical field of the invention

The present invention relates to a production method of antimicrobial coating films.

[0002]

Prior art and problems therein

A method is disclosed in Japanese Patent Hei 2[1990]-40754 for imparting an antimicrobial property to coating films to form coating films containing organic antimicrobial agents on the surface of anodic oxide films. However, although the organic antimicrobial agents are superior in the point of immediate effect, inorganic antimicrobial agents have been mainly used since the organic antimicrobial agents have problems with VOC regulation, etc., and the inorganic antimicrobial agents are superior in terms of durability, safety, etc. As to the inorganic antimicrobial agents currently being marketed, there are those obtained by carrying minute particles or ions of metals such as silver, copper, zinc, etc. as the antimicrobial component on minute inorganic particles such as zeolite, zirconium phosphate, etc.

[0003]

Incidentally, a method of imparting the antimicrobial property to coating films by adding these inorganic antimicrobial agents to aqueous electrodeposition coating materials and forming coating films has been proposed (Japanese Laid-Open Patent Hei 9[1997]-157550). Since these inorganic antimicrobial agents have a size of generally 2-10 μm and even small ones have a size of 0.3 μm, however, those which were precipitated in electrodeposition coating materials did not deposit uniformly in the coating films, or were removed by filters so that it was difficult to obtain coating films having a satisfactory antimicrobial property by the aforementioned method. Further, inferiorities such as roughening, etc. were formed in the coating films by the method above.

[0004]

At the same time, methods of imparting the antimicrobial property to the coating films by using silver colloid solutions have also been proposed. There are, for instance, a method of coating a silver colloid solution on the surface of coating films after baking and again baking them, and a method of coating a silver colloid solution on the surface of unbaked coating films and baking them. However, silver colloids are deficient in stability and the colloid itself has a size of 5-20 nm even in the smallest cases. If it is considered that colloids passing through coating films are at a level of ions such as water, etc. it is impossible for silver colloids to penetrate from the surface of coating films into the inner part of coating films. Thus, diffusion of silver into the inner part of coating films becomes only thermal diffusion in these methods and the diffusion amount of silver is extremely small, so it is difficult to impart the antimicrobial property to the bottom of very thick coating films.

[0005]

The present invention aims to provide a production method capable of obtaining coating films where silver or copper as an antimicrobial component is sufficiently and homogeneously dispersed in the inner part.

[0006]

Means for solving the problem

The present invention is characterized in that in the method for producing antimicrobial coating films, an antimicrobial aqueous solution containing silver ions or copper ions and a reducing agent is coated on the surface of unbaked coating films, followed by baking the coating films to reduce the silver ions or copper ions.

[0007]

Antimicrobial coating films are not limited only to the case of forming the antimicrobial coating films directly on the surface of base materials, but the antimicrobial coating films may [also] be formed on the coating films which are obtained by forming coating films on the surface of base materials and baking. There are no restrictions on base materials, and, for instance, iron, stainless steel, aluminum, titanium etc. are used as base materials.

[0008]

Ordinary coating specification as it is can be applied as the pretreatment of coating. The surface of base materials may be, for instance, conversion coated or anodically oxidized. Further, the pretreatment of base materials may be omitted.

[0009]

The coating materials for forming coating films are limited to water-based coating materials. As the coating method, any method of electroplating, spraying, dipping, roll coating,

brush coating, etc. may be used. Furthermore, in the case of electroplating, coating materials may be anionic resin type or cationic resin type.

[0010]

Antimicrobial aqueous solutions are prepared by dissolving metal salts including silver or copper and adding reducing agents. Preferably, these are prepared by adjusting to a weak alkali [state] of pH 7.5-9.5. As metal salts, sulfates, nitrates, chlorides, acetates, oxalates, tartrates, etc. of silver or copper are used, but the metal salts are not limited to these. The metal concentration is set at 0.001-0.1% (% by weight, hereinafter all same). As reducing agents, monosaccharides such as glucose, etc., disaccharides such as sucrose, etc., polysaccharises such as cellulose, starch, glycogen, etc., polyhydric alcohols such as ethylene glycol, propylene glycol, glycerin, etc., hydrazines such as hydrazine sulfate, hydrazine hydrate, etc., hydrides such as sodium borohydride, lithium hydride, etc., hypophosphites such as hypophorous acid, sodium hypophosphite, etc. can be used. Sulfuric acid radicals, nitric acid radicals, etc. may be removed from the antimicrobial aqueous solutions by ion exchange, etc. In this case, ethylenediamine, ethylenediamine tetraacetic acid salt, triethylenetetramine, diethylenetriamine, 1,3-diaminopropane, nitrilotriacetic acid salt, alanine, glycine, picolic acid, gelatine, etc. are used as complex forming agents. Further, anionic surfactants such as alkylbenzene sulfonic acid salt, alkyl ether sulfates, etc., and nonionic surfactants such as polyoxyethylene alkyl ether, polyethylene glycol, etc. can be used as surfactants. The adjustment to a weak alkali [state] is carried out by adding amines. Triethylamine, triethanolamine, etc. can be used as amines.

[0011]

It is preferable to carry out coating of the antimicrobial aqueous solutions on the surface of coating films by spraying or dipping. The coating amount is preferably 0.00001-0.1 g/m^2 as silver or copper.

[0012]

Coating films may be baked at the standard baking condition of coating materials to be used. Those are baked generally at 60-300°C.

[0013]

When an aqueous antimicrobial solution is coated on the surface of unbaked coating films in the present invention, silver ions or copper ions and a reducing agent in the antimicrobial aqueous solution are penetrated into the inner part of the coating films. Then, when the coating films are baked, the silver ions or copper ions are reduced to produce minute particles of silver or copper. Since silver ions or copper ions penetrate smoothly and surely into the inner part of coating films, minute particles of silver or copper are present largely not only on the surface but also in the inner part of coating films. Thus, even when the coating films are

deteriorated and the surface layer is removed, the antimicrobial property is not significatly lowered.

[0014]

Application Example of the Invention

(Application Example 1)

Formation of coating film

An electrodeposition film was formed by electrolyzing in a cationic acrylic resin type electrodeposition coating material (trade name, Aqua No. 4830 LAI, manufactured by Nippon Oils & Fats Co., Ltd.) at 50 V for 3 minutes using a hot-dip galvanized steel plate, which was pretreated with zinc phosphate, as the cathode. The target film thickness was set at 8 μm.

Preparation of antimicrobial aqueous solution

An antimicrobial aqueous solution was prepared by adding D-glucose 1.0 g to 500 ml of a silver nitrate aqueous solution containing 0.01% silver and adjusting the pH to 8 using triethylamine.

Treatment

The electrodeposited film was soaked in the antimicrobial aqueous solution for 1 minute and baked at 170°C for 30 minutes. The silver content in the electrodeposited film was analyzed and it was [found to be] 0.004 g/m^2.

[0015]

(Application Example 2)

Formation of coating film

A pure aluminum plate (A1100P-H24) was degreased, etched and smut-removed all by the ordinary method, anodized in 170 g/L sulfuric acid solution to form an anodic oxide film with a thickness of 10 μm. Then an electrodeposition film was formed by electrolyzation in an anionic acrylic-resin-type glossy electrodeposition coating material (trade name, Honnylite AL-800N, manufactured by Honny Chemical Co., Ltd.) at 120 V for 3 minutes using the anodic oxide film as the anode. The target film thickness was set at 9 μm.

Preparation of an antimicrobial aqueous solution

Nitrilotriacetic acid 0.1 g was added to 500 ml of a silver nitrate aqueous solution containing 0.005% silver, and it was passed through anion exchange resin to remove nitric acid radicals. Then, ethylene glycol 1 ml was added to the aqueous solution and its pH was adjusted to 8.5 by adding triethanolamine to prepare an antimicrobial aqueous solution.

Treatment

The electrodeposited film was coated with the antimicrobial aqueous solution using a spray gun and baked at 190°C for 30 minutes. The silver content in the electrodeposited film was analyzed and it was [found to be] 0.007 g/m^2.

[0016]

(Application Example 3)

Formation of coating film

A pure titanium plate was electrolyzed in a mixed solution of 3% phosphoric acid and 4% sulfuric acid at 60 V for 5 minutes to form a blue interference film. Then the interference film was roll-coated with a polyurethane system coating material (trade name, Anodal SP-1 liquid, manufactured by Clariant Japan K.K.) to form a coating film with a thickness of 2 μm.

Preparation of an antimicrobial aqueous solution

An antimicrobial aqueous solution was prepared in the same manner as in Application Example 2.

Treatment

The electrodeposited film was coated with the antimicrobial aqueous solution using a spray gun and baked at 80°C for 20 minutes. The silver content in the electrodeposited film was analyzed and it was [found to be] 0.005 g/m^2.

[0017]

(Application Example 4)

Formation of coating film

An aluminum alloy plate (A6063S-T5) was degreased, etched and smut-removed all by the ordinary method, then an electrodeposition film was formed by electrolyzation in a cationic acrylic-resin-type electrodeposition coating material (Aqua No.4830LAI, manufactured by Nippon Oils & Fats Co., Ltd.) at 60 V for 3 minutes using the anodic oxide film as the cathode. The target film thickness was set at 9 μm.

Preparation of an antimicrobial aqueous solution

It was prepared by adding hydrazine hydrate 1.0 ml to 500 ml of a copper acetate aqueous solution containing 0.05% copper. Furthermore, the pH was 9.1.

Treatment

The electrodeposited film was soaked in the antimicrobial aqueous solution for 3 minutes and baked at 170°C for 30 minutes. The silver content in the electrodeposited film was analyzed and it was 0.012 g/m^2.

[0018]

(Comparison Example 1)

It was carried out in the same manner as in Application Example 1 except that soaking in the antimicrobial aqueous solution was omitted.

[0019]

(Comparison Example 2)

It was carried out in the same manner as in Application Example 2 except that the antimicrobial aqueous solution was not coated.

[0020]

(Comparison Example 3)

It was carried out in the same manner as in Application Example 3 except that the antimicrobial aqueous solution was not coated.

[0021]

(Comparison Example 4)

It was carried out in the same manner as in Application Example 4 except that soaking in the aqueous antimicrobial solution was omitted.

[0022]

(Test)

On the coating films obtained in Application Examples 1-4 and Comparison Examples 1-4, respective antimicrobial ability was evaluated in accordance with the film adhesion method established by the Inorganic Antimicrobial Agent Research Society. The film adhesion method is a method of administering 0.5 ml bacteria liquid for inoculation, which is obtained by dispersing bacteria of $1x10^5$ cfu in a 1/500 ordinary nutrient broth culture medium to a 50x50 mm flat plate-form test piece, putting a polyethylene film of the same shape on it, cultivating at 35°C for 24 hours and measuring the number of surviving bacteria by the agar flat plate method. Furthermore, Escherichia Coli and yellow staphylococcus were used as the bacteria. The evaluation results for the antimicrobial ability of each coating film test piece are shown in Table 1.

[0023]

Table 1

	Number of surviving E. Coli (cfu)	Number of surviving yellow staphylococcus (cfu)
Application Example 1	<100	<100
Application Example 2	<100	<100
Application Example 3	<100	<100
Application Example 4	<100	<100
Comparison Example 1	1.5×10^5	5.2×10^5
Comparison Example 2	3.1×10^5	4.2×10^5
Comparison Example 3	2.5×10^5	1.9×10^5
Comparison Example 4	1.1×10^5	7.7×10^5

[0024]

As is clear from Table 1, in coating films of Application Examples 1-4, the number of surviving bacteria was less than 100; in other words, it was below the detection limit. In Comparison Examples 1-4, however, many bacteria remained and the antimicrobial ability was not seen.

[0025]

Effect of the invention

As explained above, since many minute particles of silver or copper can be present not only on the surface of coating films but also in the inner part of coating films according to the present invention, coating films capable of exhibiting sufficient antimicrobial ability can be obtained.